Production of Industrial Grade Silicon

Background

The production of industrial grade silicon (IGS) is vital to businesses such as the metals industry, semiconductor grade silicon manufacturing, silicones production, silicon nitrate production, and many others. In 1995, Western world demand of silicon was 790,000 metric tons. Western demand is projected to grow at an average rate of 5% into the twenty-first century. By the year 2000, this demand is expected to reach almost 1,000,000 metric tons [1]. The goal of this project is to design a grass roots facility that will safely and efficiently produce 25,000 tons per year of IGS from carbon and silicon dioxide.

Process Description

A BFD of the overall process is shown in Figure 1.

Unit 100 – Reaction Section

A PFD for Unit 100 is shown in Figure 2. Coke particles, Stream 1, and pulverized SiO_2, Stream 2, are combined and pneumatically conveyed into a refractory lined fluidized bed, H-101, where they are preheated to 1500°C. The heat is supplied to this process by the combustion of natural gas and air in the bottom portion of the vessel. At this temperature, no reaction occurs between the SiO_2 and the carbon. The off gas from H-101 is then cooled in a thermal regenerator and sent to Unit 200. The heated solids, Stream 6, are then transported to a graphite lined, electrically heated reduction furnace, R-101, where the reaction takes place and molten silicon is formed. The molten silicon is removed in Stream 14, and the unreacted SiO_2 and carbon, Stream 13, are sent to a waste treatment unit. The off gas from R-101, Stream 9, is then cooled in a thermal regenerator. Stream 10 is then compressed and mixed with Stream 8 and sent to Unit 200 as Stream 12.

Unit 200-- Co-generation Loop

A PFD for Unit 200 is shown in Figure 3. The off gases from Unit 100, Stream 12, are fed to a steam boiler, E-201, where they supply the energy to produce high-pressure steam, Stream 18. Boiler feed water, Stream 16, is pumped up to 40.8 MPa to provide the necessary pressure to produce the high-pressure steam. Stream 18 is then sent to a turbine, T-201, where electricity is generated and subsequently consumed in the process, R-101.

Once through the boiler, the cooled off gases from Unit 100, Stream 15, are sent to a fluidized bed, which contains limestone particles. Within the fluidized bed any sulfur present as sulfur dioxide in the off gas is absorbed and reacted with limestone to form calcium sulfate. The waste solids, Stream 22, are then sent to a waste treatment facility and the exiting gas is vented to the atmosphere.

Necessary Information and Simulation Hints

The reduction furnace used in this process is an electric smelting furnace, which uses three graphite electrodes to reach the necessary temperature, approximately 2045°C, for the reaction to occur. A conversion of about 90% is reached. Because carbon is consumed in the reaction, the electrodes are gradually used up and must be continually fed (replaced) to the reactor.

The following reactions lead to the production of molten silicon [2]:

$$2SiO_2(l) + 4C(s) \rightarrow SiO(g) + SiC + 3CO(g)$$

$$SiO(g) + SiC(s) \rightarrow 2Si(l) + CO(g)$$

$$SiO_2(l) + S(s) \rightarrow SO_2(g) + Si(l)$$

In order to meet environmental regulations provided by the Clean Air Act, the SO_2 must be removed. The requirement is that the off gases from this unit must contain no more than 0.5 ppm SO_2. The use of limestone in a fluidized bed significantly reduces the SO_2 present in the gas stream. With a limestone to sulfur ratio of 2.5 to 1, it has been reported that sulfur dioxide is undetectable in the exiting gas stream [3].

The limestone is fed in at the top of the fluidizing gas. The fluidizing gas consists of carbon dioxide, water vapor, nitrogen, oxygen, and sulfur dioxide. The reaction that occurs takes place between the limestone (calcium oxide) and the sulfur dioxide to yield calcium sulfate. The removal of SO_2 by limestone may be inefficient at the temperature of Stream 15. Placing the fluid bed upstream of E-201 or other methods of SO_2 removal such as caustic scrubbing should be considered.

Due to the high temperature involved, the recovery of heat from Streams 7 and 9 cannot be done in conventional heat exchangers (recuperators). For these services it is recommended that fixed bed heat regenerators be used. These regenerators take the form of packed beds of ceramic material. Operation of these units is cyclic with two units operating in parallel. Hot gas will flow through one bed while the other bed is cooled (by passing air or steam through it.) At the end of the cycle the flows are reversed with the hot gas now flowing through the cooled bed and air or steam being heated in the bed of hot solids. Additional heat recovery from the air and steam will allow additional utility savings.

Equipment Summary

C-101	Compressor
E-101A/B	Thermal Regenerator
E-102A/B	Thermal Regenerator
H-101	Fluidized Bed Preheater
R-101	Reduction Furnace
E-201	Steam Boiler
P-201A/B	Boiler Feed Water Pump
R-201	Fluidized Bed Scrubber
T-201	Turbine

References

1. "Silicon," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., vol. 21, 1997, pp. 1110-1111.

2. Nagamuri, N., I. Malinsky, & A. Claveau, "Thermodynamics of the Si-C-O System for the Production of Silicon Carbide and Metallic Silicon," Metallurgical Transactions, **17B**, 503-514, (Sept. 1986).

3. Peterson, V., G. Daradimos, H. Serbent, and H. Schmidt, Combustion in the Circulating Fluid Bed: An Alternative Approach in Energy Supply and Environmental Protection, U.S. Dept. Of Energy, April 9-11, 1980.

Stream Tables for IGS Production

Stream	1	2	3	4	5	6
Temp. (°C)	25	25	25	25.0	25	1500
Press. (atm)	1	1	1	2.0	2	1
Total Flow (kg/h)	3071	7382	10453	363.7	7965	10453
Component Flows (kg/h)						
Silicon Dioxide	--	7382	7382	--	--	7382
Silicon	--	--	--	--	--	--
Carbon	3071	--	3071	--	--	3071
Natural Gas	--	--	--	363.7	--	--
Oxygen	--	--	--	--	1856	--
Nitrogen	--	--	--	--	6109	--
Carbon Dioxide	--	--	--	--	--	--
Water	--	--	--	--	--	---

Stream	7	8	9	10	11	12
Temp. (°C)	1500.0	600.0	2045	480	600	600.0
Press. (atm)	1.5	1.5	1	1	1.5	1.4
Total Flow (kg/h)	8328.0	8328.0	9745	9745	9745	18073.0
Component Flows (kg/h)						
Silicon Dioxide	--	--	--	--	--	--
Silicon	--	--	--	--	--	--
Carbon	--	--	--	--	--	--
Natural Gas	--	--	--	--	--	--
Oxygen	428	428	--	--	--	428
Nitrogen	6109	6109	--	--	--	6109
Carbon Dioxide	1019	1019	9745	9745	9745	10764
Water	772	772	--	--	--	772

Stream	13	14	15	16	17	18
Temp. (°C)	2045	2045	260.0	85.0	85.0	194.7
Press. (atm)	1	1	1.5	5.4	40.8	40.8
Total Flow (kg/h)	1605	3100	18073.0	14967.0	14967.0	14967.0
Component Flows (kg/h)						
Silicon Dioxide	738	--	--	--	--	--
Silicon	--	3100	--	--	--	--
Carbon	867	--	--	--	--	--
Natural Gas	--	--	--	--	--	--
Oxygen	--	--	428	--	--	--
Nitrogen	--	--	6109	-	--	--
Carbon Dioxide	--	--	10764	--	--	--
Water	--	--	772	14967	14967	14967

Stream	19	21	22
Temp. (°C)	100	260	260.0
Press. (atm)	1	1	1.0
Total Flow (kg/h)	14967	18073	184.3
Component Flows (kg/h)			
Silicon Dioxide	--	--	--
Silicon	--	--	--
Carbon	--	--	--
Natural Gas	--	--	--
Oxygen	--	428	--
Nitrogen	--	6109	--
Carbon Dioxide	--	10764	--
Water	14967	772	--

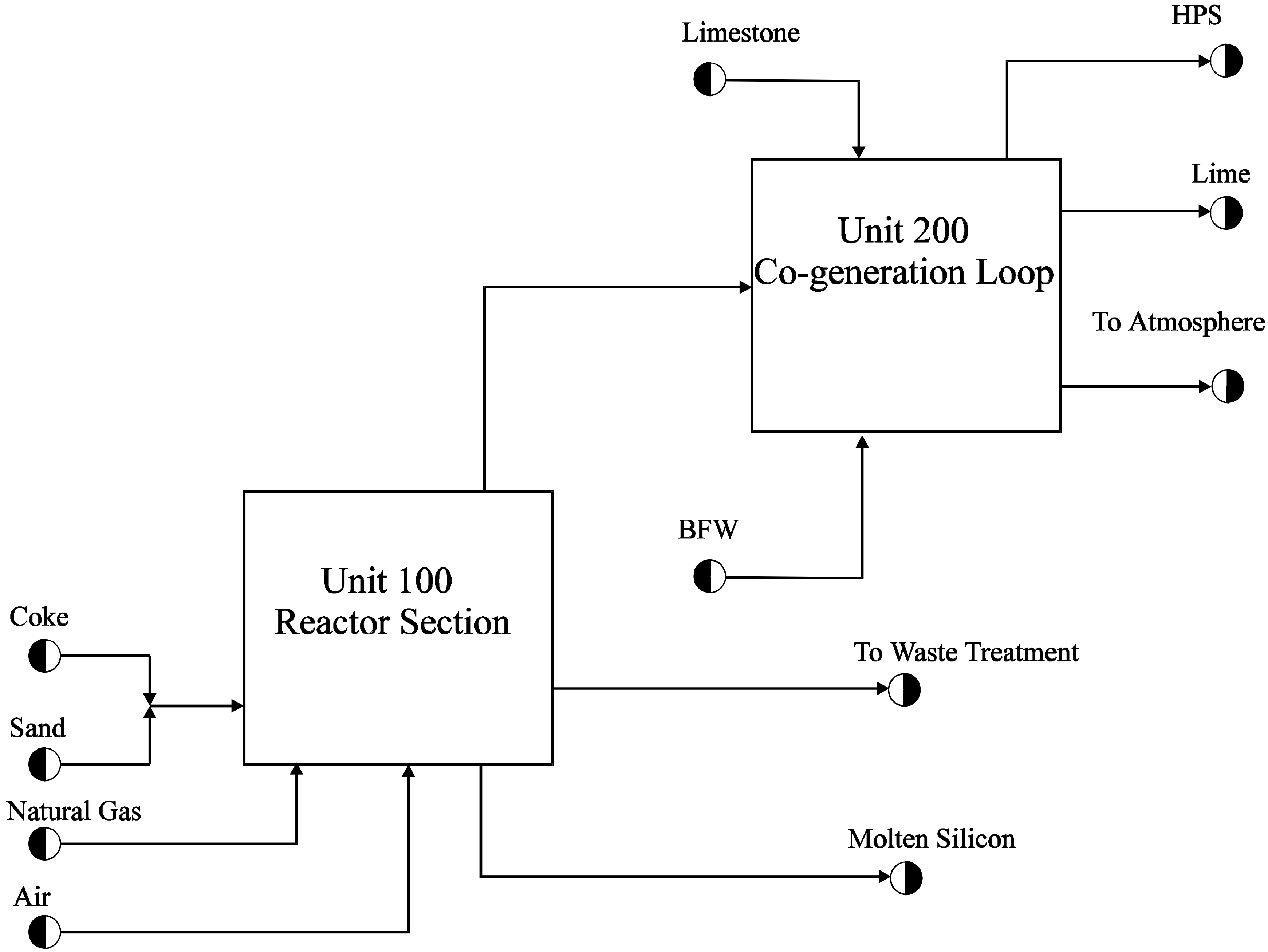

Figure 1: BFD for Production of Industrial Grade Silicon

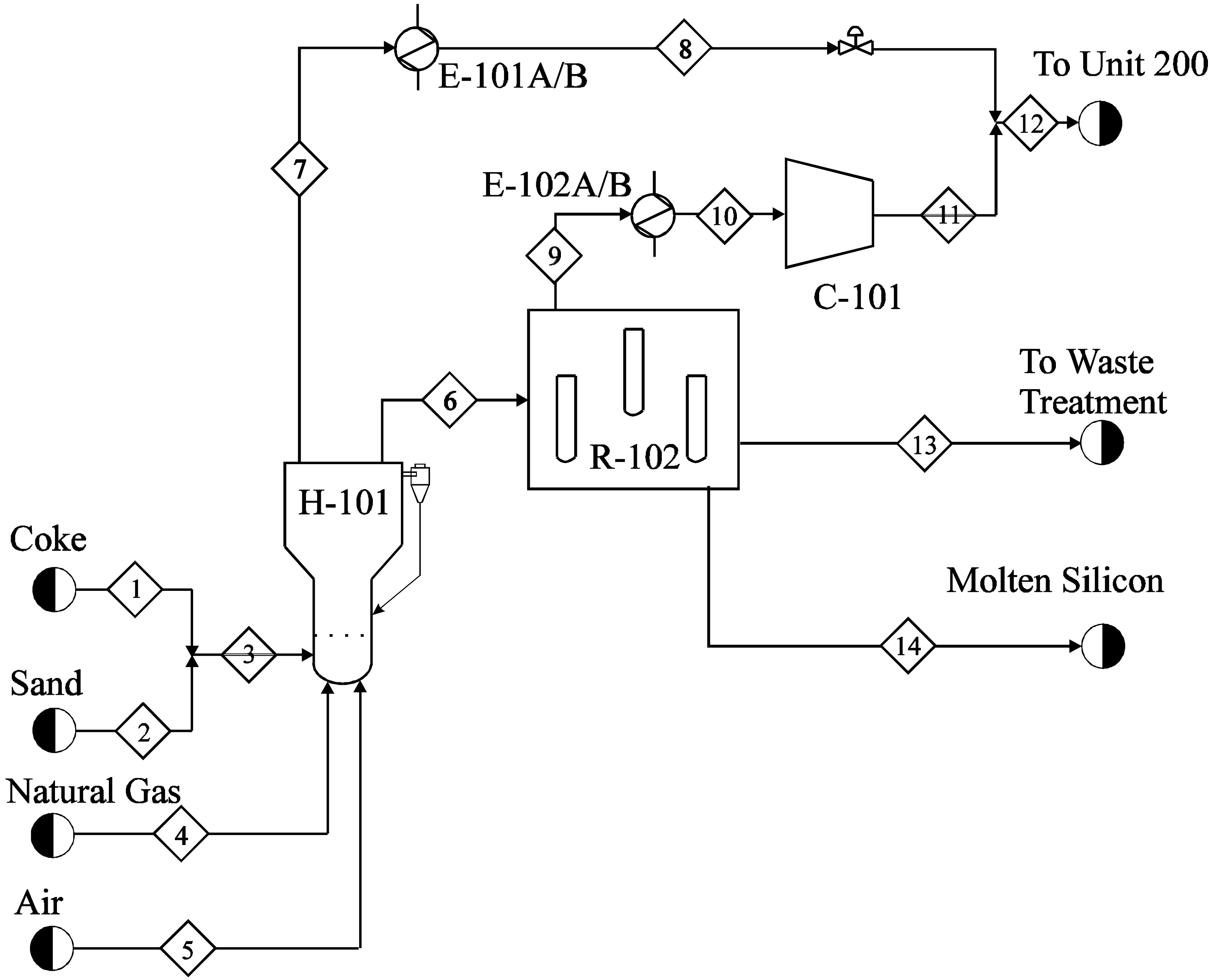

Figure 2: PFD for Unit 100 -- Reaction Section

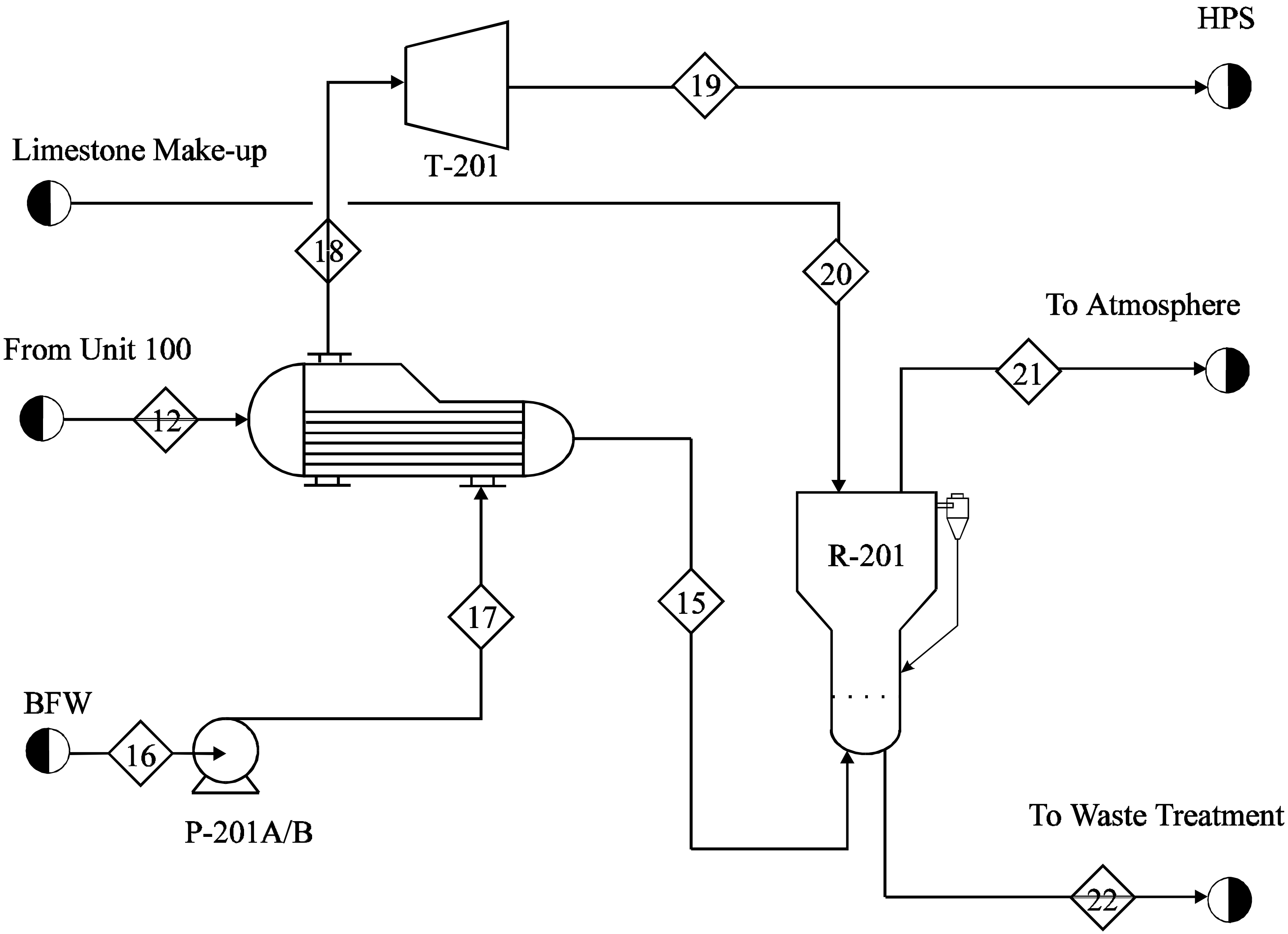

Figure 3: PFD for Unit 200 -- Cogeneration Loop